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ORIGINAL PAPER

Molecular and isotopic compositions and origin of natural gases from Cambrian and Carboniferous-Lower Permian reservoirs of the onshore Polish Baltic region

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Abstract Natural gases from Middle Cambrian and Carboniferous-Lower Permian reservoirs of the onshore Polish Baltic region were studied for their molecular and stable isotope compositions. The following gas species were analysed: $^{12,13}C$ in CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10} and CO_2, $^{1,2}H$ in CH_4, $^{14,15}N$ in N_2, and stable isotopes of all noble gases. Due to significantly different geological settings and genetic types of source rocks of Eastern and Western Pomerania, the molecular and isotopic compositions of natural gases of these two regions exhibit distinct differences. Hydrocarbon gases associated with oil accumulated in the Middle Cambrian reservoir of Eastern Pomerania were generated during low-temperature thermogenic processes from a single source rock containing Type-II kerogen at one phase of petroleum generation. Non-associated hydrocarbon gases accumulated in the Carboniferous (Mississippian and Pennsylvanian)-Lower Permian (Rotliegend) reservoirs of Western Pomerania originated during at least two phases of gas generation by thermogenic processes from mainly Type-III kerogen and a small component of mixed Type-III/II kerogen. Noble gases are in general heavily enriched in radiogenic and nucleogenic isotopes such as ^4He, ^{40}Ar and ^{21}Ne accumulated in the reservoirs. Weak contributions of mantle-derived He and Ne are observed. Radiogenic $^4He/^{40}Ar$ ratios are higher than the average production rate ratio of about 5 for radiogenic $^4He/^{40}Ar$ in crustal materials, which might have been caused by a selective supply of ^4He that is lighter than ^{40}Ar from crustal rocks, or (U + Th)/K ratio might be higher than the average in crustal block. Carbon dioxide from gases of both the Western and Eastern Pomerania were mainly generated during thermogenic processes of transformation of organic matter, although gases of Western Pomerania can contain an endogenic component. Molecular nitrogen from the Eastern Pomeranian natural gases was mainly generated during low-temperature thermal transformation of organic matter and derived from NH_3 and NH_4 of crustal fluid, whereas molecular nitrogen from Western Pomeranian natural gases contains a significant component from the destruction of organic matter at a higher maturity level which may have been caused by a high heat flux from the volcanic activity during late Pennsylvanian–early Rotliegend ages, and has a bigger component release from NH_4-rich illites.

Keywords Origin of natural gases · Hydrocarbon gases · Noble gases · Carbon dioxide · Molecular nitrogen · Stable isotopes

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Introduction

This study aims to determine the origin of hydrocarbon and non-hydrocarbon components of natural gases of the onshore Polish Baltic region based on the molecular composition and stable carbon isotope compositions of methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane and carbon dioxide, stable hydrogen isotope composition of methane, stable nitrogen isotope composition of molecular nitrogen (N_2), and stable isotope composition of all noble gases (helium, neon, argon, krypton and

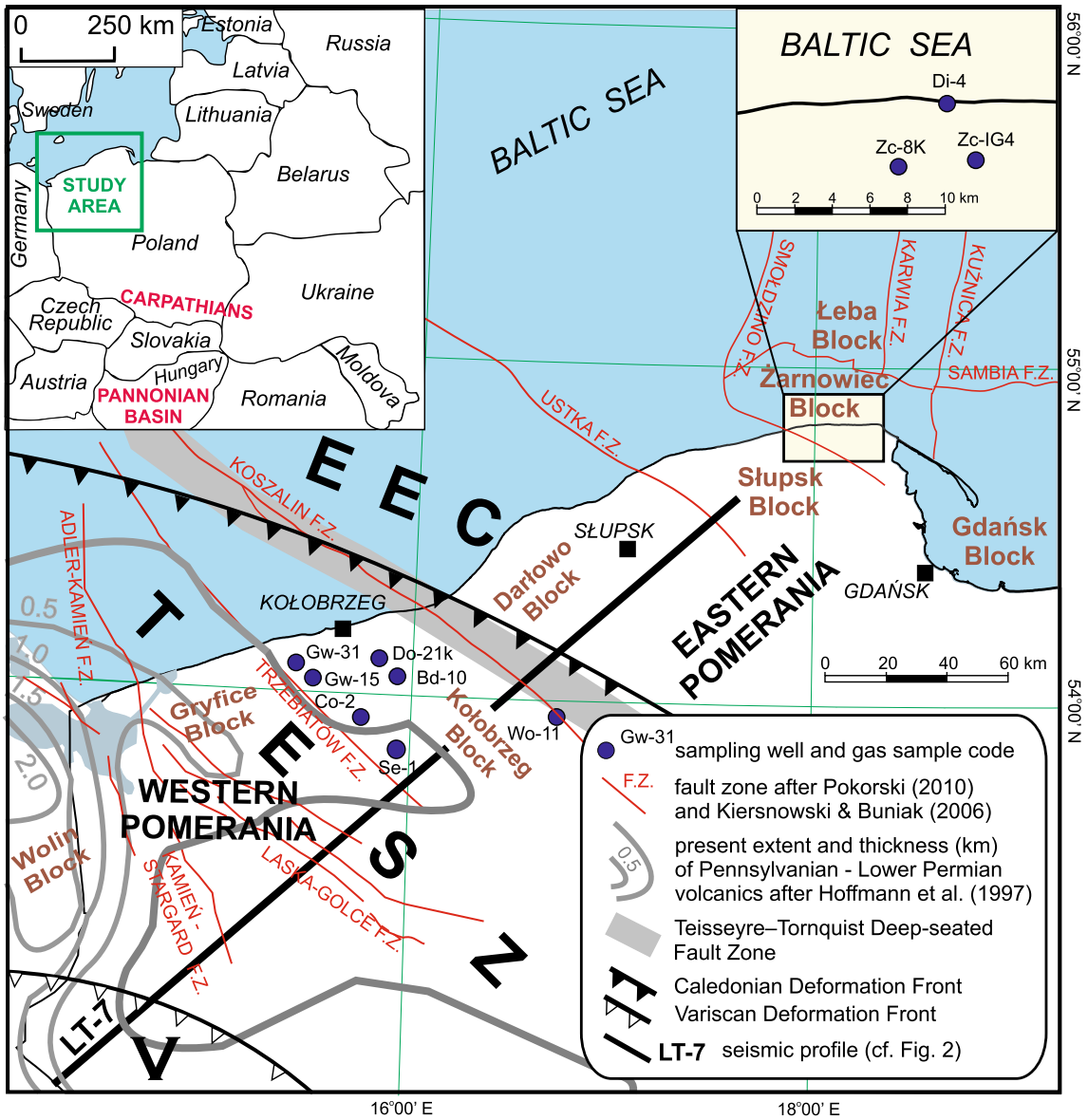

Fig. 1 Sketch tectonic map of the NW part of Poland with the location of gas sampling sites. *V* Variscides, *TESZ* Trans-European Suture Zone, *EEC* East European Craton. Geology after Dadlez et al. (2005), Hoffmann et al. (1997), Kiersnowski and Buniak (2006), Nawrocki and Poprawa (2006) and Pokorski (2010)

xenon). Three samples were collected from Middle Cambrian reservoir in the Eastern Pomerania and seven samples from Carboniferous (Mississippian and Pennsylvanian) and Lower Permian (Rotliegend) reservoirs in the Western Pomerania of the Baltic region (Fig. 1).

The Polish part of the Baltic region is located within the contact zone between two large geologic units: Precambrian Platform (East European Craton) and Palaeozoic Platform. These two units are juxtaposed at the Teisseyre–Tornquist Zone, separating the Precambrian Platform, which comprises Eastern Pomerania from the Palaeozoic Platform, with Western Pomerania inside (Figs. 1, 2). For this reason, the petroleum systems must be considered separately in Eastern and Western Pomerania (Karnkowski et al. 2010). Since 1955, the Polish Baltic region has been explored for conventional (oil and gas) hydrocarbons, and more recently also for unconventional (shale gas and shale oil) hydrocarbons in Eastern Pomerania.

Kotarba (1998) and Kotarba et al. (2005) attempted to explain the origin of natural gas accumulations in the Mississippian, Pennsylvanian and Rotliegend reservoirs in Western Pomerania. Hydrocarbon (methane, ethane and propane) gases and carbon dioxide mainly originated from Type-III kerogen with a small component of Type-II kerogen in two

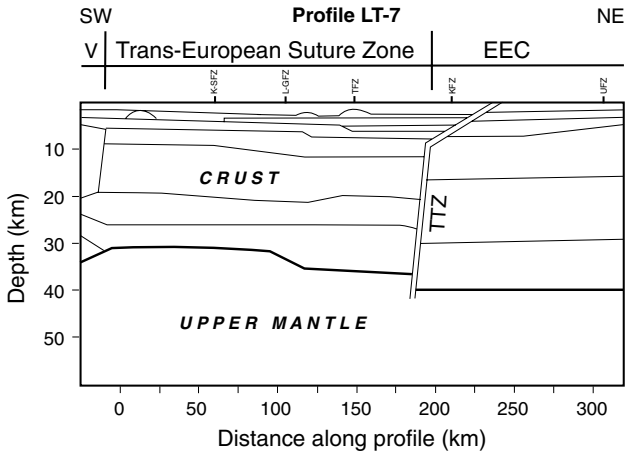

Fig. 2 Schematic cross section showing the crustal structure along the LT-7 seismic location profile. Modified after Dadlez et al. (2005), Grad et al. (2002) and Guterch et al. (1994). *TTZ* Teisseyre-Tornquist deep-seated Fault Zone, *EEC* East European Craton, *V* Variscides, *K-SFZ* Kamień-Stargard Fault Zone, *L-GFZ* Laska-Golce Fault Zone, *TFZ* Trzebiatów Fault Zone, *KFZ* Koszalin Fault Zone, *UFZ* Ustka Fault Zone

stages. Based on stable carbon isotope composition of these gases, established the first stage within the oil window and the second within the gas window (Kotarba et al. 2005). Molecular nitrogen also was generated during thermogenic processes of organic matter transformation, and probably partly in abiogenic processes (Gerling et al. 1998; Kotarba et al. 2005). Taking into consideration the closeness of the Polish and Ukrainian Carpathian region and Pannonian Basin in Hungary from the study area (Fig. 1), the origin of hydrocarbon and non-hydrocarbon gases from these basins is compared for comparison's sake (Kotarba and Nagao 2008; Cornides et al. 1986; Ballentine et al. 1991).

Organic geochemistry analyses (Kotarba et al. 2004) reveal that the best source rocks of terrestrial Type-III kerogen occur within the Tournaisian (Mississippian) strata where the present TOC content is up to 10.7 wt%. Moreover, the same type of organic matter occurs within the Visean (Mississippian) and Westphalian (Pennsylvanian) strata where the present TOC contents are up to 2.6 and 2.2 wt%, respectively.

Kotarba (2010) and Kotarba and Lewan (2013) made the first attempts to explain the origin of natural gases accumulated in the Middle Cambrian reservoir in onshore and offshore areas of Eastern Pomerania based on hydrous pyrolysis experiments. On the basis of these results, Kotarba and Lewan (2013) concluded that hydrocarbon gases and carbon dioxide were generated within the oil window from Type-II kerogen. No isotopic studies of noble gases in natural gases accumulated in the Middle Cambrian and Carboniferous-Lower Permian reservoirs in the Baltic region, which could explain their origin, were carried out.

Several potential source rock horizons are present in the Lower Palaeozoic (Cambrian, Ordovician and Silurian) succession (Burchardt and Lewan 1990; Buchardt et al. 1998; Więcław et al. 2010a, b; Zdanaviciute and Lazauskiene 2004). The Upper Cambrian and Lower Ordovician (Tremadocian) strata contain the best source rocks, with low-organic sulphur, oil-prone Type-II kerogen and initial total organic carbon (TOC) contents up to 18 and 20 wt%, respectively (Buchardt et al. 1998; Więcław et al. 2010a, b; Kosakowski et al. 2010). Caradocian (Ordovician) strata can be considered as an additional source of hydrocarbons, the initial TOC for which ranges between 1 and 6 wt%, respectively. The Llandovery (Silurian) strata reveal moderate and locally high hydrocarbon potential of source rocks, for which the present TOC content reaches locally 10 wt% (usually 1–2 wt%) (Więcław et al. 2010a, b). Hydrous pyrolysis experiments (Kotarba and Lewan 2013) reveal that the Llandovery source rocks are not contributors to the natural gas accumulations in the Middle Cambrian reservoirs. However, Silurian organic-rich facies are potential rocks for shale gas and shale oil (e.g. Poprawa 2010; Karnkowski et al. 2010; Kotarba and Lewan 2013).

Geological setting and petroleum occurrence

The Trans-European Suture Zone (TESZ) is a tectonic zone 150–200 km wide, which separates the East European Craton from Variscan orogenic belt (Fig. 1). The provenance and accretionary history of the crustal blocks involved in the TESZ are still under discussion (e.g. Dadlez et al. 2005; Nawrocki and Poprawa 2006; Pharaon 1999). The Teisseyre–Tornquist Fault Zone (TTZ) is the north-eastern faulted boundary of TESZ (Dadlez et al. 2005) and is deep rooted in the upper mantle (Fig. 2).

Eastern Pomerania is subdivided into three tectonic blocks: Darłowo Block in the west, Słupsk Block in the middle and Żarnowiec Block in the east (Fig. 1). Eastern Pomerania is in the southern part of the Baltic Basin. The Baltic Basin (also called Peribaltic Syneclise) is a large, roughly NE–SW trending depression on the NW margin of the Precambrian East European Craton formed by pericratonic subsidence during the Caledonian diastrophic-sedimentation cycle (Brangulis et al. 1992; Poprawa et al. 1999; Ulmishek 1990; Witkowski 1989) (Fig. 1).

The Baltic Basin was affected by Proterozoic tectonism (early Ediacaran rifting) as well as by the Caledonian collision, Permo–Triassic rifting, late Jurassic and late Cretaceous uplifts (Ulmishek 1990; Poprawa 2006; Poprawa et al. 1999, 2006). In the southern part of the Baltic Basin, the Lower Palaeozoic sedimentary sequence prevails containing Silurian strata up to 3,000 m thick (Modliński and Podhalańska 2010). The Upper Cambrian strata are

represented by black bituminous shales with thin interbeds and lenses of dark, often bioclastic limestones (Modliński and Podhalańska 2010). The Upper Cambrian–Tremadocian Alum Shales are mainly black organic-rich mudstones (Burchardt and Lewan 1990) and Llandovery strata contain claystones and mudstones. Their thickness in the Polish part of the Baltic region varies from 10 to 100 m (Modliński and Podhalańska 2010).

Onshore petroleum exploration in the Polish Baltic region began in 1955 (Karnkowski 1999a). In 1970, a small Żarnowiec oil deposit was first discovered within the Middle Cambrian sandstone reservoir in the Eastern Pomerania area, while three small accumulations of oil were discovered at Dębki in 1971, Białogóra in 1991, and gas-condensate at Żarnowiec-West in 1987 (Karnkowski 1999a; Karnkowski et al. 2010).

Western Pomerania is subdivided into three tectonic blocks: the Wolin Block in the west, the Gryfice Block in the middle and the Kołobrzeg Block in the east (Fig. 1). The Adler–Kamień, Kamień–Stargard, Trzebiatów and Koszalin fault zones are deeply rooted in the Proterozoic crystalline basement (Pokorski 2010). The main structural features of Western Pomerania are determined by the consolidated Caledonian basement. In vertical succession, the following rock complexes are distinguished: Caledonian (Silurian, Ordovician and Cambrian), epi-Caledonian (Devonian and Mississippian), the Pennsylvanian-Lower Permian (Westphalian–Rotliegend), the Upper Permian (Zechstein)-Mesozoic and the Cenozoic (Karnkowski et al. 2010). The allochthonous Lower Palaeozoic complex overlies Palaeoproterozoic crystalline rocks. At the end of Silurian, this complex underwent intense thrust-and-fold deformation (Podhalańska and Modliński 2006; Pokorski 2010). In early Devonian, a large part of the study area was an eroded continent.

Depositional history restarted at the end of Emsian or in the beginning of Eifelian (Lipiec and Matyja 1998; Matyja 2009). Deposition continued in the middle and late Devonian (Karnkowski et al. 2010; Matyja 2006, 2009). In the Mississippian, Western Pomerania was an area of deep (clastics) and shallow (carbonates) shelf (Żelichowski, 1987). Volcanic activity, registered at the turn of the Devonian and Mississippian and marine deposition, terminated in the early Namurian (Karnkowski et al. 2010). During the entire Namurian and early Westphalian time, the Devonian–Carboniferous deposits of Pomerania were eroded and denudated exposing the underlying units. In middle Westphalian, the black and grey continental clastics with thin coal interbeds accumulated. In late Westphalian, the red intercalations occurred. The Stephanian deposits in the Pomerania continued into the Autunian (Lower Permian) (Pokorski 1990; Żelichowski 1987). Sedimentation of Rotliegend clastic sequences (Pokorski 1990) started after a prolonged stratigraphic hiatus, during which the Devonian, Mississippian and Pennsylvanian strata were removed from the Precambrian Platform. The Kołobrzeg Block, and to a smaller degree the Gryfice Block, was also uplifted and eroded.

In Western Pomerania, the volcanics (andesite, ignimbrite, rhyolite and tuff) of late Stephanian–early Rotliegend (Autunian) ages are preserved (Hoffmann et al. 1997; Karnkowski 1999b; Pokorski 1990). The thickest sections (over 2 km) are observed in the Wolin Block. In the western part of the Gryfice Block, the maximum thickness was about 600 m, and in the eastern part of this block close to Trzebiatów Fault Zone, only 100 m of section is present (Fig. 1). In the Kołobrzeg Block, there are only isolated remnants of effusive and pyroclastic rocks to 238.5 m of thickness (Pokorski 1990).

Twelve gas fields were discovered within the Mississippian, Pennsylvanian and Rotliegend strata in the Western Pomerania area: one in Wierzchowo (in 1977) in Mississippian, five in Wrzosowo (in 1977), Gorzysław N (in 1976), Gorzysław S (in 1976), Trzebusz (in 1978) and Daszewo N (in 1981) in Pennsylvanian, and six in Międzyzdroje E (in 1970), Międzyzdroje W (in 1970), Przytór (in 1971), Białogard (in 1985), Ciechnowo (in 1993) and Sławoborze (in 2001) in Rotliegend sandstone reservoirs (Karnkowski 1999a; Karnkowski et al. 2010; Nasiadka 2008).

Details of the geology and petroleum occurrence in the Polish Baltic region were published by Aizberg et al. (1997); Brangulis et al. (1992), Dadlez et al. (2005), Grad et al. (2002), Guterch et al. (1994); Hoffmann et al. (1997), Kanev et al. (1994), Karnkowski (1999a), Karnkowski et al. (2010), Kiersnowski and Buniak (2006), Matyja (2006), Modliński and Podhalańska (2010), Podhalańska and Modliński (2006), Pokorski (2010), Poprawa et al. (1997, 2006, 2010), Schleicher et al. (1998), Witkowski (1989), and references therein.

Sampling procedure

Three natural gas samples from wells Di-4, Zc-8k and Zc-IG4 producing from the Middle Cambrian sandstone reservoirs in Eastern Pomerania, and seven samples from wells Bd-10, Co-2, Do-21k, Gw-15, Gw-31, Se-1 and Wo-11, producing from the Carboniferous-Lower Permian sandstone reservoirs in Western Pomerania were collected for this study (Fig. 1). Mississippian, Pennsylvanian and Rotliegend free gases were collected directly at the well head in a metal container (~1,000 cm^3), and Middle Cambrian gases dissolved in oil and condensate from separators in a glass container (~500 cm^3) (Table 1). Gas samples for noble gas analysis were collected and stored in a metal container (~30 cm^3) with a metal valve, at pressures higher than 1 atm to prevent possible leakage of atmospheric air

Table 1 Location of sampling wells

Well	Sample code	Field name	Stratigraphy of reservoir	Reservoir depth (m b.s.l.)	Type of accum	Coordinates	
						Latitude (N)	Longitude (E)
Eastern Pomerania							
Dębki-4	Di-4	Dębki	M Cambrian	2,678–2,728	o Assoc	54°49'54″	18°06′12″
Żarnowiec-8k	Zc-8k	Żarnowiec	M Cambrian	2,811–2,828	o Assoc	54°48′01″	18°03′36″
Żarnowiec-IG4	Zc-IG4	Żarnowiec W	M Cambrian	2,740–2,755	c Assoc	54°48′20″	18°07′15″
Western Pomerania							
Wierzchowo-11	Wo-11	Wierzchowo	Miss	3,163–3,200	Gas	53°53′09″	16°36′20″
Gorzysław-15	Gw-15	Gorzysław S	Pen	2,756–2,812	Gas	54°03′33″	15°20′51″
Gorzysław-31	Gw-31	Gorzysław N	Pen	2,707–2,800	Gas	54°05′51″	15°19′01″
Daszewo-21k	Do-21k	Daszewo	Pen	3,226–3,254	Gas	54°07′12″	15°47′08″
Białogard-10	Bd-10	Białogard	Pen&Rotl	3,125–3,180	Gas	54°02′57″	15°56′18″
Ciechnowo-2	Co-2	Ciechnowo	Rotl	3,736–3,780	Gas	53°51′51″	15°42′54″
Sławoborze-1	Se-1	Sławoborze	Rotl	3,628–3,659	c Assoc	53°53′55″	15°41′23″

Miss Mississippian, *Pen* Pennsylvanian, *Rotl* Rotliegend, *M* Middle, *o* oil, *c* condensate, *assoc* associated, *accum* accumulation, *b.s.l.* below surface level

into the container. General information on the locations of the sampling sites is given in Table 1 and shown in Fig. 1.

Analytical procedure

Molecular compositions of natural gases (CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, *i*-C_5H_{12}, *n*-C_5H_{12}, *neo*C_5H_{12}, C_6H_{14}, C_6H_{14}, CO_2, O_2, H_2, N_2, He, Ar) were analysed in a set of columns on Hewlett Packard 5890 Series II, Fisons Instruments 8000 and Carlo Erba 6000 gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors.

Stable carbon, hydrogen and nitrogen isotope analyses were performed using Finnigan Delta Plus and Micromass VG Optima mass spectrometers. The stable carbon isotope data are expressed in the δ-notation ($\delta^{13}C$, ‰) relative to VPDB on a scale such that NBS-22 (oil) is −30.03 ‰. The stable hydrogen isotope data are reported in δ-notation (δ^2H, ‰) relative to the international standard, Vienna Standard Mean Ocean Water (VSMOW = 0.0 ‰), and normalized to standard light arctic precipitation SLAP (2-point calibrations) as recommended by Coplen (2011). Analytical precision is estimated to be ±0.2 and ±3 ‰, respectively. Methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane and *n*-pentane were separated chromatographically for stable carbon isotope analyses. They were direct combusted over hot copper oxide (850 °C) produced by the online system and then transmitted to a mass spectrometer (GC–IRMS method). Water resulting from the combustion of methane for stable hydrogen isotope analyses was reduced to molecular hydrogen (H_2) with zinc (Florkowski 1985). The result of stable nitrogen isotope analysis is presented in the δ-notation ($\delta^{15}N$, ‰) relative to air nitrogen standard. Analytical precision is estimated to be ±0.4 ‰. Molecular nitrogen was separated chromatographically for stable nitrogen isotope analysis and was transmitted to the mass spectrometer via the online system. Molecular composition and stable carbon, hydrogen and nitrogen isotope compositions were measured in the Laboratory of Petroleum and Isotopic Geochemistry at the AGH University of Science and Technology in Kraków.

Noble gas isotopic composition and concentration were measured with a system for noble gas mass spectrometry in the Geochemical Research Center at the University of Tokyo following the procedure in Kotarba and Nagao (2008). Part of gas was introduced into a gas pipette (5.82 cm^3) connected to a noble gas purification line, and pressure and temperature of the gas were measured to calculate the absolute amount (in unit of cm^3STP). The known volume of gas was introduced into the noble gas purification line. These noble gases were then purified by exposing them to two Ti–Zr getters heated at about 800 °C. The purified noble gases were separated into three fractions He, Ne and Ar–Kr–Xe for the first step by adsorbing Ar, Kr and Xe on to a charcoal trap cooled by liquid nitrogen. Residual Ar, Kr and Xe in the gaseous phase of He and Ne were removed by adsorbing them onto another charcoal trap. Because of the extremely high abundance ratios of He/Ne (>10,000), special care was taken to separate He and Ne before analyses. When the amount of He in the purification line was ~10^{-3} cm^3STP, Ne was adsorbed on a cryogenically cooled trap at the temperature of 15 K, then reduction in ~1/10,000 was applied for He by using a small volume in the purification line before isotope analysis of He. After finishing the He analysis, Ne was released from the trap at 50 K for isotope analysis.

In the analysis of Ar isotopic ratio, as well as concentrations of Ar, Kr and Xe, all Ar, Kr and Xe were released from

Table 2 Molecular composition of analysed natural gases

Sample code	Molecular composition (vol%)													
	CH_4	C_2H_6	C_3H_8	*i*-C_4[a]	*n*-C_4[b]	*neo*-C_5	*i*-C_5[c]	*n*-C_5[d]	C_{6+}[e]	N_2	CO_2	H_2	He[f]	Ar[g]
Eastern Pomerania														
Di-4	76.1	12.8	6.79	0.40	0.96	0.003	0.053	0.054	0.016	1.75	0.88	0.00	0.12	0.01
Zc-8k	77.7	11.6	5.34	0.43	1.26	0.005	0.079	0.060	0.051	2.50	0.83	0.00	0.11	0.007
Zc-IG4	84.1	9.46	3.39	0.26	0.67	0.002	0.062	0.072	0.052	0.76	0.93	0.00	0.11	0.006
Western Pomerania														
Wo-11	55.0	1.25	0.12	0.05	0.08	0.009	0.044	0.048	0.057	43.1	0.03	0.01	0.14	0.007
Gw-15	42.1	0.69	0.07	0.02	0.02	0.008	0.012	0.003	0.016	56.6	0.14	0.00	0.22	0.02
Gw-31	45.9	0.84	0.09	0.03	0.05	0.014	0.020	0.007	0.025	52.7	0.03	0.00	0.20	0.02
Do-21k	64.7	1.01	0.08	0.03	0.05	0.009	0.013	0.012	0.020	33.7	0.17	0.00	0.10	0.008
Bd-10	48.5	0.80	0.06	0.01	0.03	0.006	0.007	0.007	0.013	50.3	0.02	0.00	0.15	0.01
Co-2	48.8	1.42	0.57	0.09	0.11	0.015	0.052	0.054	0.014	48.5	0.14	0.01	0.15	0.01
Se-1	51.1	0.73	0.42	0.31	0.29	0.019	0.24	0.19	0.21	46.1	0.10	0.00	0.13	0.02

[a] *i*-C_4H_{10}
[b] *n*-C_4H_{10}
[c] *i*-C_5H_{12}
[d] *n*-C_5H_{12}
[e] $C_{6+} = C_6H_{14} + C_7H_{16}$
[f] From Table 4
[g] From Table 4

the charcoal trap at ca. 200 °C, and were purified again and measured for ^{40}Ar, ^{84}Kr and ^{132}Xe, and then measured for Ar isotopic ratios. When Kr and Xe isotopic ratios were measured in addition to Ar isotopes, Ar, Kr and Xe were separated before introduction into the mass spectrometer by using the cryogenic trap at the temperatures of 100, 150 and 230 K.

Sensitivities and mass discrimination correction factors of the mass spectrometer system were determined by measuring known amounts of atmosphere with the same procedure applied for samples. The discrimination factor for $^3He/^4He$ was determined by measuring the HESJ (He Standard of Japan) with $^3He/^4He = (28.88 \pm 0.14) \times 10^{-6}$ (Matsuda et al. 2002). Experimental uncertainties for the noble gas concentrations were estimated to be about 10 % based on the reproducibility of measurements of the standard gas and ambiguity in the gas reduction procedure.

Results and discussion

Hydrocarbon gases

Eastern Pomerania

The hydrocarbon gases from the Middle Cambrian reservoirs of Eastern Pomerania vary insignificantly in both their molecular and isotopic compositions (Tables 2, 3; Figs. 3, 4, 5) and show that the Middle Cambrian gases of Eastern Pomerania are genetically related to thermogenic processes. These gases, similar as gases from the Carpathian region (Kotarba and Nagao 2008), reveal normal isotopic order $\delta^{13}C(CH_4) < \delta^{13}C(C_2H_6) < \delta^{13}C(C_3H_8)$ (Figs. 3 and 4a) as reported by Chung et al. (1988). Natural gases from the Carpathian region except thermogenic gases also contain microbial ones (Figs. 3, 4, 5). Gases from the both Carpathian and Eastern Pomerania basins are genetically associated with oil.

In Fig. 4a, b, the vitrinite reflectance curves are fitted after mode of Berner and Faber (1996, 1997) based on average $\delta^{13}C = -29.0$ ‰ for Ordovician Type-II kerogen (Więcław et al. 2010a). However, hydrous pyrolysis experiments of gas generation simulation and calibration of gas isotope models for Upper Cambrian–Tremadocian source rocks (Kotarba and Lewan 2013) reveal that isotope curves on both $\delta^{13}C(C_2H_6)$ versus $\delta^{13}C(CH_4)$ (Fig. 4a) and $\delta^{13}C(C_3H_8)$ (Fig. 4b) diagrams should be shifted to new positions for the Middle Cambrian gases as compared to curves from Berner and Faber (1996, 1997). This shift is mainly caused by the isotopic composition of the source, and to a lesser extent by thermal maturation (Kotarba and Lewan 2013). These normal linear trends indicate that the analysed Middle Cambrian gases were generated from only one source rock containing Type-II kerogen (Fig. 3) at maturity corresponding to 0.5 to 0.7 % vitrinite reflectance

Table 3 Molecular indices and stable carbon, hydrogen and nitrogen isotope composition of analysed natural gases

Sample code	Indices							Stable isotopes (‰)									
	C_{HC}^{a}	CH_4/C_2H_6	C_2H_6/C_3H_8	$C_3H_8/\sum C_4^{b}$	C_3H_8/C_{4+}^{c}	$i\text{-}C_4H_{10}/n\text{-}C_4H_{10}$	CDMI[d]	$\delta^{13}C$ (CH_4)	$\delta^{2}H$ (CH_4)	$\delta^{13}C$ (C_2H_6)	$\delta^{13}C$ (C_3H_8)	$\delta^{13}C$ ($i\text{-}C_4$)[e]	$\delta^{13}C$ ($n\text{-}C_4$)[f]	$\delta^{13}C$ ($i\text{-}C_5$)[g]	$\delta^{13}C$ ($n\text{-}C_5$)[h]	$\delta^{13}C$ (CO_2)	$\delta^{15}N$ (N_2)
Eastern Pomerania																	
Di-4	3.9	5.94	1.89	5.01	53.9	0.41	1.14	−47.8	−214	−38.8	−33.0	−31.6	−31.1	n.a.[i]	n.a.	−2.2	−12.4
Zc-8k	4.6	6.70	2.17	3.17	27.5	0.34	1.06	−46.9	−211	−38.4	−32.5	−31.6	−31.0	−30.8	−30.2	−1.2	−12.9
Zc-IG4	6.5	8.89	2.79	3.62	18.0	0.39	1.09	−47.4	−206	−37.5	−32.7	−31.8	−31.4	−30.7	−30.6	−0.5	−12.8
Western Pomerania																	
Wo-11	40.3	44.0	10.9	0.87	0.72	0.70	0.05	−29.5	−119	−33.2	−28.2	−25.7	−26.5	n.a.	n.a.	−7.7	8.8
Gw-15	55.5	61.0	10.1	1.84	1.74	0.69	0.33	−29.5	−117	−31.7	−27.5	−24.9	−25.8	n.a.	n.a.	−13.7	5.2
Gw-31	49.3	54.6	9.30	1.19	1.39	0.63	0.07	−29.6	−123	−30.5	−23.2	−24.0	−22.3	n.a.	n.a.	−16.4	6.3
Do-21k	59.2	64.1	12.3	1.11	1.53	0.62	0.26	−29.4	−123	−28.3	−25.7	−22.6	−22.8	n.a.	n.a.	−12.7	11.2
Bd-10	56.6	60.6	14.2	1.38	1.70	0.31	0.04	−27.9	−115	−29.3	−27.5	n.a.	n.a.	n.a.	n.a.	−6.7	10.6
Co-2	24.6	34.4	2.50	2.89	4.21	0.84	0.29	−28.5	−122	−28.1	−23.7	−23.4	−23.0	n.a.	n.a.	−6.8	5.6
Se-1	44.3	70.0	1.73	0.71	0.64	1.08	0.20	−31.1	−125	−28.0	−24.4	−25.8	−24.1	−25.1	−25.9	−7.9	5.2

n.a. not analysed

[a] $C_{HC} = CH_4/(C_2H_6 + C_3H_8)$

[b] $\sum C_4 = i\text{-}C_4H_{10} + n\text{-}C_4H_{10}$

[c] $C_{4+} = i\text{-}C_4H_{10} + n\text{-}C_4H_{10} + i\text{-}C_5H_{12} + n\text{-}C_5H_{12} + neoC_5H_{12} + C_6H_{14} + C_7H_{16}$

[d] $CDMI = [CO_2/(CO_2 + CH_4)] * 100\ (\%)$

[e] $i\text{-}C_4 = i\text{-}C_4H_{10}$

[f] $nC_4 = nC_4H_{10}$

[g] $i\text{-}C_5 = i\text{-}C_5H_{12}$

[h] $n\text{-}C_5 = n\text{-}C_5H_{12}$

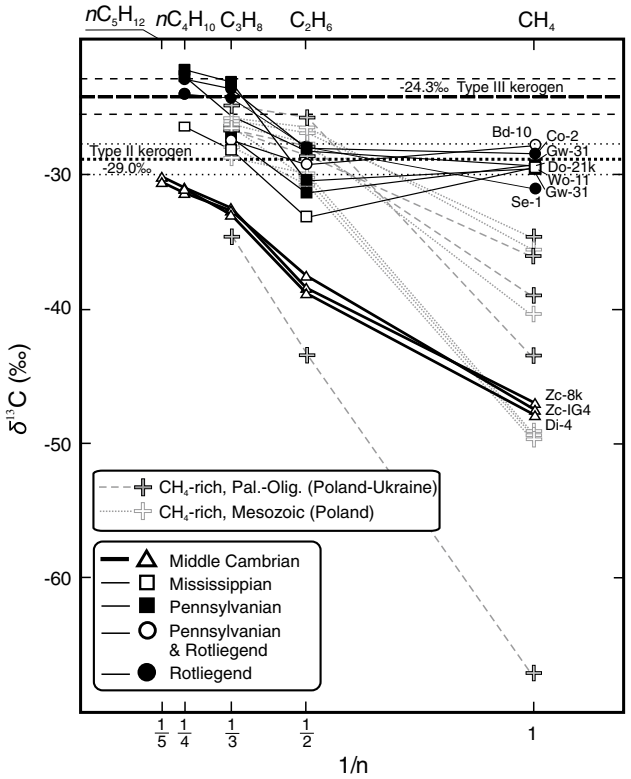

Fig. 3 Stable carbon isotope composition of methane, ethane, propane, *n*-butane and *n*-pentane versus the reciprocal of their carbon number for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. Structure of the *graph* for methane, ethane and propane after Rooney et al. (1995). Position of curves based on average $\delta^{13}C = -29.0$ ‰ (16 samples, standard deviation 1.0 ‰) for Upper Cambrian and Tremadocian Type-II kerogen (Więcław et al. 2010a) and average $\delta^{13}C$ values $= -24.3$ ‰ (10 samples, SD 1.3 ‰) for Mississippian and Pennsylvanian (clastic) Type-II kerogen (Kotarba et al. 2004; Więcław et al. 2011). Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

scale (Fig. 4a). These gases are genetically associated with oil (Fig. 5).

Source rocks in the Eastern Pomerania mainly occur within the Upper Cambrian–Tremadocian strata (Więcław et al. 2010a; Kotarba and Lewan 2013) (Fig. 6a). Reservoir rocks occur within the Middle Cambrian strata and seal the rocks within the upper part of the Lower and Upper Silurian strata. Oil and natural gas migrated from Upper Cambrian–Tremadocian source rocks to Middle Cambrian reservoir through Smołdzino, Karwia and Kuźnica fault zones (Fig. 1). Overburden was formed by Triassic, Jurassic and Cretaceous rocks (Fig. 6a). The traps were formed at the end of Caledonian orogeny at the turn of Silurian and Devonian, and rejuvenated during Variscan orogeny at the turn of Pennsylvanian and Permian. Consideration of stable isotopic compositions of gaseous hydrocarbons allowed for determining the generation and expulsion, and migration and accumulation periods, and critical point of Palaeozoic–Cenozoic petroleum system (Fig. 6a).

Western Pomerania

The hydrocarbon gases from the Mississippian, Pennsylvanian and Rotliegend reservoirs of Western Pomerania vary in both their molecular and isotopic compositions compare to gases of Eastern Pomerania (Tables 2, 3; Figs. 3, 4, 5). Both molecular and isotopic compositions (Tables 2, 3; Figs. 3, 4, 5) show that these gases are genetically related to thermogenic decomposition of mainly Type-III kerogen and small components of mixed Type-III/II kerogen (Fig. 5a). $\delta^{13}C$ values of hydrocarbon gases are shown in a reciprocal carbon number plot in Fig. 3. In this plot, all natural gases from the Mississippian, Pennsylvanian and Rotliegend reservoirs of the Western Pomerania show the concave (so-called dogleg) trends (Zou et al. 2007), which are different from the more linear trends reported by Chung et al. (1988) and Rooney et al. (1995). The reversed stable carbon isotope trend $\delta^{13}C(C_2H_6) > \delta^{13}C(C_3H_8)$ of some analysed natural gases from the Mississippian, Pennsylvanian and Rotliegend reservoirs of the Western Pomerania also occurs in conventional and unconventional gases in Poland (Wielkopolska and Lower Silesia regions), USA, Canada and China (Burruss and Laughrey 2010; Dai et al. 2004, 2005; Kotarba et al. 2014, Tittley and Muehlenbachs 2013; Tittley et al. 2011; Xia et al. 1999, 2013; Zumberge et al. 2012). Zou et al. (2007) suggest that a concave trend, exemplified by relatively ^{13}C depleted methane and enriched propane as compared to ethane, results from a natural gas that was not generated from a single source rock or that underwent post-generation alteration (e.g. secondary gas cracking, microbial oxidation, thermochemical sulphate reduction). However, results from hydrous pyrolysis experiments (Kotarba et al. 2009; Kotarba and Lewan 2013) show that a "dogleg" trend can be generated from a single source and that it is irrespective of kerogen type. No abiogenic methane is observed in the composition of analysed gases (Fig. 5b). In Fig. 4a, b, the vitrinite reflectance curves are fitted after mode of Berner and Faber (1996, 1997) based on average $\delta^{13}C$ values $= -24.8$ ‰ for Mississippian and Pennsylvanian (clastic) Type-III kerogen (Kotarba et al. 2004; Więcław et al. 2011).

The position of the Mississippian, Pennsylvanian and Rotliegend gases of Western Pomerania in Fig. 4a, b shifts from both Berner and Faber, and hydrous pyrolysis trends in Fig. 4a, b as well as "dog-leg" trends in Fig. 3 suggest that at least two phases of gas generation took place: the first one at the stage of 0.7 to 0.9 % and the second one at the stage of 1.5 to 2.0 % maturity of source rocks in the

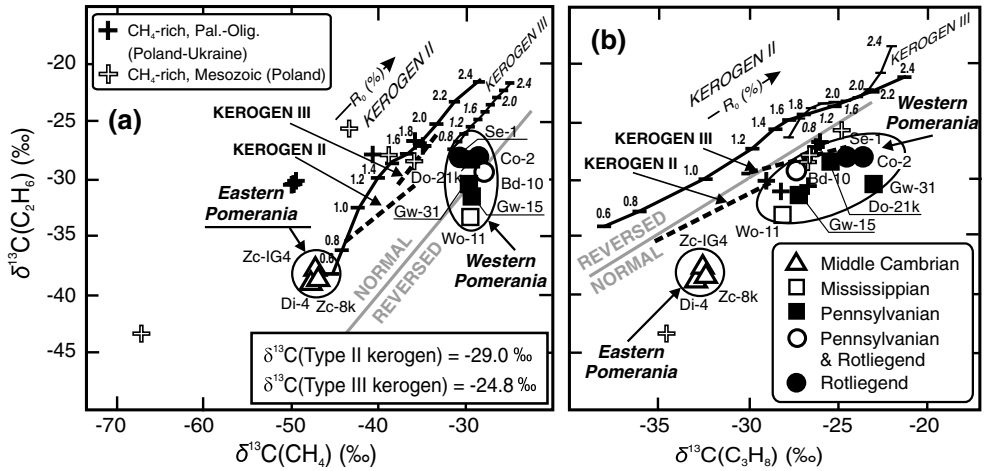

Fig. 4 $\delta^{13}C(C_2H_6)$ versus **a** $\delta^{13}C(CH_4)$ and **b** $\delta^{13}C(C_3H_8)$ for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. Position of vitrinite reflectance curves marked as continuous lines of Type-II and Type-III kerogens (**a**, **b**) after mode of Berner and Faber (1996). These curves were shifted based on average $\delta^{13}C = -29.0$ ‰ for Upper Cambrian and Tremadocian Type-II kerogen (Więcław et al. 2010a) and average $\delta^{13}C$ values $= -24.8$ ‰ for Mississippian and Pennsylvanian (clastic) Type-III kerogen (Kotarba et al. 2004; Więcław et al. 2011). *Curves* for Type-III and combined Types-I/II, Type-II and Type-IIS kerogens from hydrous pyrolysis (Kotarba et al. 2009) marked as *dashed* and *thickened lines* of Types-III kerogen and Type-II kerogens on respective **a** and **b** diagrams. Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

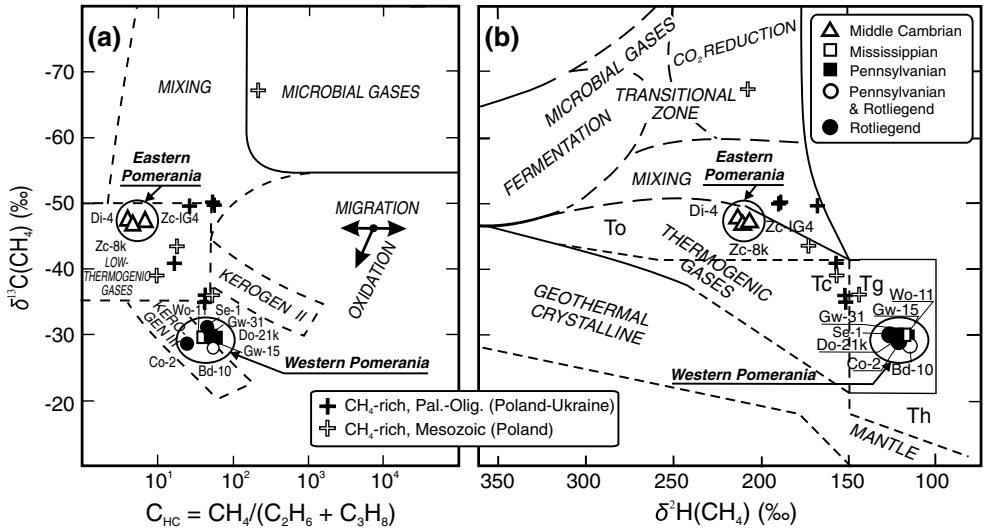

Fig. 5 $\delta^{13}C$ of methane versus **a** hydrocarbon index C_{HC} (i.e. $CH_4/[C_2H_6 + C_3H_8]$) and **b** δ^2H of methane for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. Compositional fields are modified by authors from **a** Whiticar (1994) and **b** Whiticar et al. (1986) and Hosgormez et al. (2008). *To* thermogenic associated with oil, *Tc* thermogenic associated with condensate, *Tg* high-temperature thermogenic ("gas window"), *Th* thermogenic with high-temperature CO_2–CH_4 equilibrium (Welham 1988). Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

vitrinite reflectance scale, demonstrating a possible connection with structural evolution of Western Pomerania.

Gaseous hydrocarbons were probably generated from source rocks within the Pennsylvanian (Wesphalian) and Lower Carboniferous (Visean) strata (Fig. 6b) (Grotek et al. 1998; Kotarba et al. 2004; Matyasik 1998). Reservoir rocks occur within the Mississippian, Pennsylvanian and Rotliegend strata and seal rocks within the Permian (Rotliegend and Zechstein) strata (Fig. 6b). Natural gas migrated from source rocks to reservoirs through Adler–Kamień–Stargard,

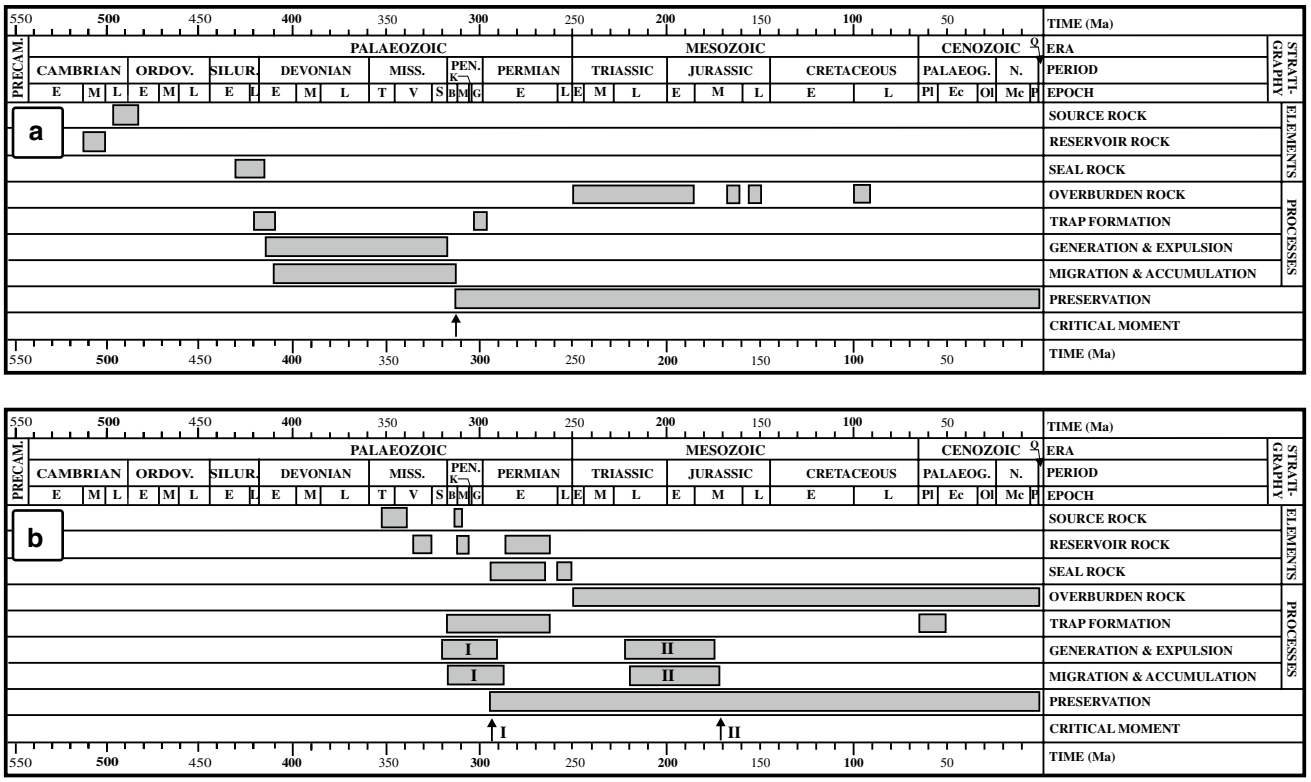

Fig. 6 Event charts of the Palaeozoic–Mesozoic–Cenozoic petroleum systems of **a** Eastern and **b** Western Pomerania. I—first stage of hydrocarbon generation, expulsion, migration and accumulation processes, and first critical moment; II—second stage of hydrocarbon generation, expulsion, migration and accumulation processes, and second critical moment; *PRECAM.* Precambrian, *ORDOV.* Ordovician, *MISS.* Mississippian, *T* Tournaisian, *V* Visean, *S* Serpuhovian, *PEN.* Pennsylvanian, *B* Bashkirian, *M* Moscovian, *K* Kasimovian, *G* Gzhelian, *PALAEOG.* Palaeogene, *N* Neogene, *Q* Quaternary, *Pl* Palaeocene, *Ec* Eocene, *Ol* Oligocene, *Mc* Miocene, *P* Pliocene, *E* Early, *M* Middle, *L* Late

Laska–Golce, Trzebiatów and Koszalin fault zones (Figs. 1, 2). Overburden was formed by a full sequence from Triassic to Quaternary rocks (Fig. 6b). Traps within the Mississippian, Pennsylvanian and Rotliegend strata were formed at the end of Variscan orogeny at the turn of Pennsylvanian and Permian, and rejuvenated during Laramian orogenic phase at the turn of Cretaceous and Palaeogene. Consideration of stable isotopic compositions of gaseous hydrocarbons created bases for determining two independent generation and expulsion, and migration and accumulation periods, and thus two independent critical points (Fig. 6b).

Non-hydrocarbon gases

Noble gases

The very high $^{4}He/^{20}Ne$ ratios ranging from 148,000 to 174,000 and from 33,800 to 76,300 in Eastern and Western Pomerania, respectively (Table 4) were measured. The $^{4}He/^{20}Ne$ ratios more than 5 orders of magnitude higher than the atmospheric value of 0.32 confirm the negligible contamination of the gases with atmospheric noble gases throughout the procedures of gas collection, storage in the metal sample bottles and mass spectrometry. High concentrations of ^{4}He (952–2,200 ppm) and low $^{3}He/^{4}He$ ratios ranging from 0.031×10^{-6} to 0.086×10^{-6} observed for all the samples imply that the He is mostly derived from crustal materials enriched in ^{4}He produced through radioactive decay of uranium and thorium. Concentrations of other noble gases ^{20}Ne, $^{36,\ 40}Ar$, ^{84}Kr and ^{132}Xe are very low as compared to those of atmosphere (Table 4). Their relative elemental abundances (Table 5) are similar to those of atmospheric noble gases dissolved in water, i.e. progressively enriched in heavier noble gas elements. Deep-sea and subaerial sediments have noble gases enriched in heaver noble gases, reflecting enrichments in heavy noble gases in water (e.g. Ozima and Podosek 2002). Noble gases in the gas samples studied in this work were probably incorporated into the source regions of natural gases with groundwater or with fossil sea water during the formation of the sedimentary rocks. The relatively low concentrations of Ne, Ar, Kr and Xe would have been caused by dilution with the gaseous hydrocarbons and nitrogen (Table 2). Large contributions of radiogenic ^{40}Ar are also observed

Table 4 Noble gas concentrations and isotopic ratios of He, Ne and Ar

Sample code	Isotopes											
	^{4}He (ppm)	^{3}He/^{4}He 10^{-6}	^{20}Ne (ppm)	^{20}Ne/^{22}Ne	^{21}Ne/^{22}Ne	^{36}Ar (ppm)	^{40}Ar (ppm)	^{38}Ar/^{36}Ar	^{40}Ar/^{36}Ar	^{84}Kr (ppm)	^{132}Xe (ppm)	^{4}He/^{20}Ne
Eastern Pomerania												
Di-4	1,210	0.0432 ± 0.0063	0.0082	9.211 ± 0.025	0.07409 ± 0.00051	0.0357	112.7	0.1910 ± 0.0020	3,155 ± 11	0.00180	0.000197	148,000
Zc-8k	1,130	0.0307 ± 0.0090	0.0065	9.361 ± 0.036	0.07801 ± 0.00082	0.0242	65.6	0.1900 ± 0.0014	2,708 ± 10	0.00120	0.000132	174,000
Zc-IG4	1,140	0.0335 ± 0.0072	0.0066	9.319 ± 0.018	0.07503 ± 0.00038	0.0268	58.7	0.1925 ± 0.0028	2,194 ± 9	0.00129	0.000115	173,000
Western Pomerania												
Wo-11	1,350	0.0362 ± 0.0074	0.0400	9.695 ± 0.014	0.04098 ± 0.00044	0.1015	99.7	0.1888 ± 0.0007	982 ± 2	0.00405	0.000310	33,800
Gw-15	2,200	0.0530 ± 0.0065	0.0320	9.539 ± 0.016	0.06757 ± 0.00026	0.0934	233.0	0.1904 ± 0.0017	2,494 ± 13	0.00358	0.000158	68,800
Gw-31	2,010	0.0507 ± 0.0043	0.0351	9.633 ± 0.019	0.04823 ± 0.00025	0.0961	168.1	0.1900 ± 0.0011	1,749 ± 6	0.00363	0.000321	57,200
Do-21k	952	0.0855 ± 0.0071	0.0178	9.694 ± 0.013	0.04277 ± 0.00055	0.0573	79.8	0.1901 ± 0.0013	1,393 ± 6	0.00237	0.000200	53,500
Bd-10	1,510	0.0724 ± 0.0045	0.0293	9.727 ± 0.018	0.04617 ± 0.00019	0.0791	136.5	0.1909 ± 0.0010	1,726 ± 5	0.00311	0.000263	51,400
Co-2	1,540	0.0382 ± 0.0078	0.0201	9.780 ± 0.014	0.05318 ± 0.00027	0.0624	136.1	0.1908 ± 0.0012	2,180 ± 9	0.00253	0.000259	76,300
Se-1	1,310	0.0431 ± 0.0058	0.0235	9.557 ± 0.013	0.06999 ± 0.00019	0.0807	200.0	0.1908 ± 0.0019	2,479 ± 8	0.00318	0.000173	55,500
Air[a]	5.24	1.4	16.5	9.80	0.0290	31.5	9,300	0.1880	296.0	0.649	0.0234	0.318

[a] After Ozima and Podosek (2002)

in all the samples as high ^{40}Ar/^{36}Ar ranging from 980 to 3,160.

As noted above, He is mostly of radiogenic origin. This interpretation is illustrated in Fig. 7, where ^{3}He/^{4}He ratios for the samples are plotted against ^{4}He/^{20}Ne ratios. The very high ^{4}He/^{20}Ne of 1×10^{6} assumed for the upper mantle and the crust is due to the observed high ratios up to 174,000 (for Zc-8k) for the samples (Table 4). The lines connecting air—upper mantle and air—crust in Fig. 7 are mixing lines. Three data points with high ^{3}He/^{4}He (Fig. 7) are from CO_2-rich gas in Hungary (Cornides et al. 1986), indicating mantle He contribution. On the other hand, the data points plotting in the lower left area dominated by radiogenic ^{4}He mostly derived from a crustal source. Moreover, the plots show variable contributions of He from crustal, mantle and atmospheric sources related to the sampling localities. However, appreciable amount of ^{3}He can be produced through a nuclear reaction $^{6}\mathrm{Li(n, \alpha)}^{3}\mathrm{H} \rightarrow {}^{3}\mathrm{He} + \beta^{-}$ in Li-rich crustal materials. The relatively high ^{3}He/^{4}He ratios observed for the samples such as Do-21k and Bd-10 might have been resulted by addition of the Li-related ^{3}He product, because very high concentrations of Li up to several hundred ppm in Rotliegend brines from the North German Basin have been reported by Lüders er al. (2010).

Figure 8 is a plot of ^{20}Ne/^{22}Ne versus ^{21}Ne/^{22}Ne ratios. Effects of nucleogenic Ne isotopes are significant in excess of ^{21}Ne and ^{22}Ne due to the nuclear reactions such as $^{18}\mathrm{O}(\alpha, n)^{21}\mathrm{Ne}$, $^{19}\mathrm{F}(\alpha, n)^{22}\mathrm{Na}(\beta^{+})^{22}\mathrm{Ne}$, $^{19}\mathrm{F}(\alpha, p)^{22}\mathrm{Ne}$ and $^{24,25}\mathrm{Mg}(n, \alpha)^{21,22}\mathrm{Ne}$ (Wetherill 1954; Yatsevich and Honda 1997). As the production ratio ^{21}Ne/^{22}Ne is variable depending on ^{18}O/^{19}F ratio within a range of α-particles, the trend in Fig. 8 is from natural gases and brines in North America (Kennedy et al. 1990).

In contrast to most Carpathian gases plotting below a mixing line between atmospheric and nucleogenic Ne (Kotarba and Nagao 2008), all data for Pomeranian gases are plotted above the "Nucleogenic Ne" line (Fig. 8). Ne isotopic ratios for the samples from Eastern Pomerania and Western Pomerania are clearly separated into two groups, and the contribution of nucleogenic Ne is larger for the former than the latter. The difference may be due to different concentrations of Ne in these gases, i.e. ^{20}Ne concentrations are of the order of 10^{-3} and 10^{-2} ppm for Eastern and Western Pomerania, respectively. The Ne isotopic compositions of the samples studied in this work can be explained by adding the upper mantle Ne to the source region, which increased ^{20}Ne/^{22}Ne to 10–11, then adding of nucleogenic Ne. As a small contribution of mantle He is observed in the samples as noted above, trace amounts of mantle-derived Ne could be introduced into the source regions of the samples along with mantle He. Similar Ne isotopic ratios were also observed for the Ta-17 sample from Tarnów gas field in the Polish Carpathian region (Kotarba and Nagao 2008),

Table 5 Elemental abundance patters

Sample code	Indices				
	F(4)	F(20)	F(36)	F(84)	F(132)
Eastern Pomerania					
Di-4	204,000	0.436	1	2.45	7.55
Zc-8k	281,000	0.513	1	2.40	7.47
Zc-IG4	257,000	0.470	1	2.35	5.86
Western Pomerania					
Wo-11	80,200	0.752	1	1.94	4.18
Gw-15	142,000	0.654	1	1.86	2.32
Gw-31	126,000	0.696	1	1.83	4.58
Do-21k	100,000	0.593	1	2.01	4.78
Bd-10	115,000	0.706	1	1.91	4.56
Co-2	148,000	0.616	1	1.97	5.68
Se-1	97,500	0.556	1	1.91	2.94

$F(m) = ({}^{m}X/{}^{36}Ar)_{sample}/({}^{m}X/{}^{36}Ar)_{air}$; where ^{m}X stands ^{4}He; ^{20}Ne; ^{36}Ar; ^{84}Kr and ^{132}Xe

for which we offered a similar explanation. The Ne isotopic ratios for Eastern Pomerania, however, may be interpreted by only a contribution of nucleogenic Ne with higher $^{21}Ne/^{22}Ne$ production ratio in a condition of high O/F abundance ratio. The dashed line to (1, 0) in Fig. 8 indicates an addition of Ne with isotopic ratios $^{21}Ne/^{22}Ne = 1$ and $^{20}Ne/^{22}Ne = 0$ to atmospheric Ne, which may explain the data from Eastern Pomerania. On the other hand, addition of almost pure ^{21}Ne to atmospheric Ne is needed to produce observed Ne data for Western Pomerania, which is difficult to produce ^{21}Ne only in naturally occurring crustal materials. As the Rotliegend brines from the North German Basin noted above also contain high concentrations of Br and Cl (and probably F) (Lüders et al. 2010), negligible contribution of nucleogenic ^{22}Ne from F is unlikely. The presence of Pennsylvanian-Lower Permian volcanic locks beneath Western Pomerania as shown in Fig. 1 would be a possible source of Ne of mantle origin.

Concentrations of radiogenic ^{4}He and ^{40}Ar and excess ^{21}Ne in the samples defined in caption for Fig. 9 are summarized in Table 6. The excess ^{21}Ne is mostly nucleogenic in origin as discussed above. Concentrations of radiogenic ^{40}Ar and nucleogenic ^{21}Ne are compared with radiogenic ^{4}He concentrations in Fig. 9a, b, in which the concentrations in gas samples from the Carpathian region (Kotarba and Nagao 2008) have been plotted for comparison's sake. The concentrations of radiogenic ^{4}He and ^{40}Ar, and nucleogenic ^{21}Ne in most samples studied in this work are higher

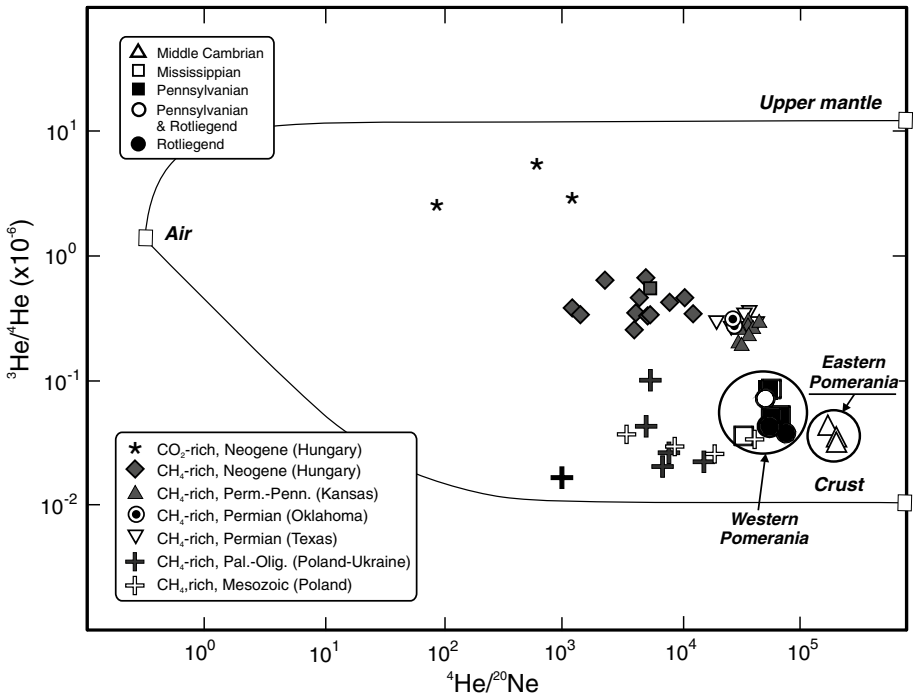

Fig. 7 $^{3}He/^{4}He$ versus $^{4}He/^{20}Ne$ ratios for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. The following values for end members have been adopted: air ($^{3}He/^{4}He = 1.4 \times 10^{-6}$, $^{4}He/^{20}Ne = 0.318$) (Ozima and Podosek 2002), mid-oceanic ridge basalts (MORB) representing upper mantle ($^{3}He/^{4}He = 12 \times 10^{-6}$, $^{4}He/^{20}Ne = 1{,}000{,}000$) (e.g. Graham 2002), and old continental crust ($^{3}He/^{4}He = 0.01 \times 10^{-6}$, $^{4}He/^{20}Ne = 1{,}000{,}000$) (Ballentine and Burnard 2002). Data reported for gas fields in USA (Ballentine and Sherwood Lollar 2002), for Pannonian Basin, Hungary (Cornides et al. 1986; Ballentine et al. 1991) and for Polish and Ukrainian Carpathian region (Kotarba and Nagao 2008). *Pal.* Palaeocene, *Olig.* Oligocene

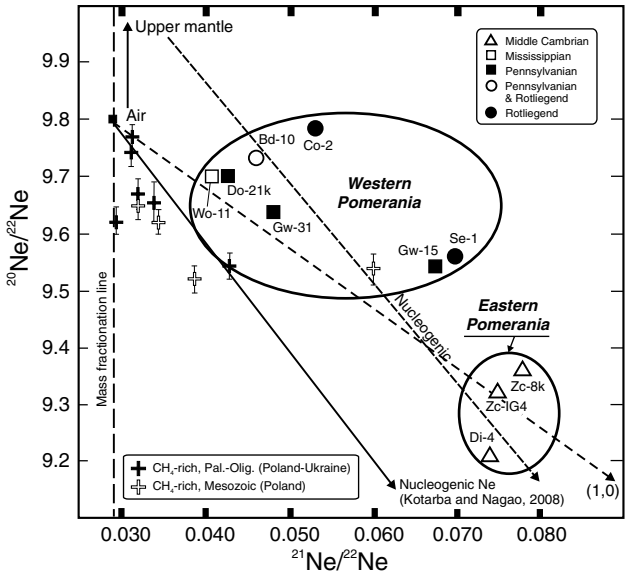

Fig. 8 $^{20}Ne/^{22}Ne$ versus $^{21}Ne/^{22}Ne$ ratios for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. The mass fractionation line from atmospheric Ne, addition of nucleogenic Ne ($^{20}Ne/^{22}Ne = 0.3$ and $^{21}Ne/^{22}Ne = 0.47$: e.g. Kennedy et al. 1990; Sherwood Lollar et al. 1994; Ozima and Podosek 2002), and addition of upper mantle Ne ($^{20}Ne/^{22}Ne = 12.2$ and $^{21}Ne/^{22}Ne \approx 0.055$: Graham 2002; Ballentine et al. 2005) are indicated. Data reported for the Polish and Ukrainian Carpathian region are from Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

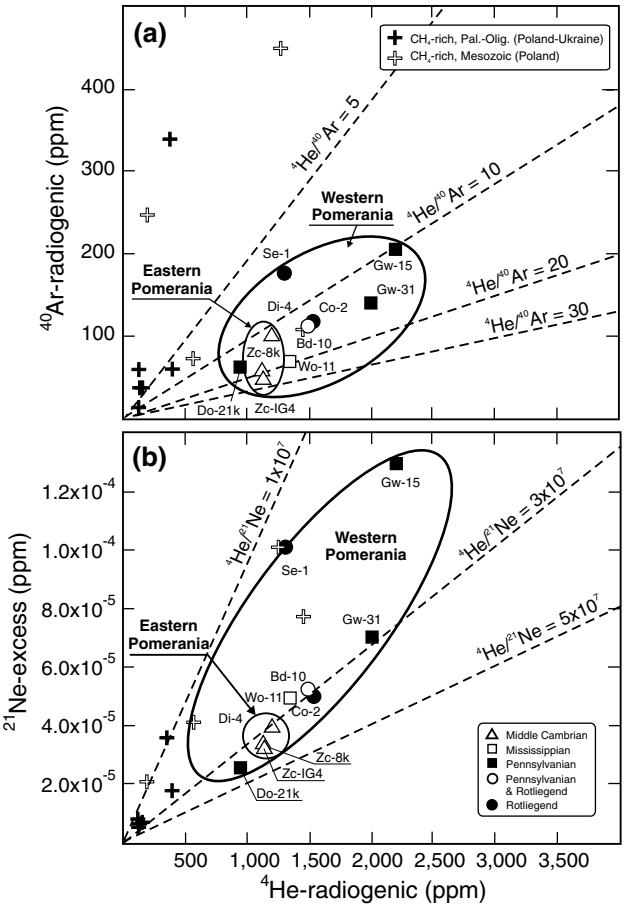

Fig. 9 **a** Radiogenic ^{40}Ar and **b** excess ^{21}Ne versus radiogenic ^{4}He for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. Data reported for gas fields in the Polish and Ukrainian Carpathian region (Kotarba and Nagao 2008). Concentration of radiogenic ^{40}Ar is defined by $[^{40}Ar\text{-rad}] = [(^{40}Ar/^{36}Ar)_{sample} - (^{40}Ar/^{36}Ar)_{air}] \times [^{36}Ar_{sample}]$, where $(^{40}Ar/^{36}Ar)_{air} = 296$. Concentration of excess ^{21}Ne is calculated with the formula, $[^{21}Ne\text{-excess}] = [(^{21}Ne/^{22}Ne)_{sample} - (^{21}Ne/^{22}Ne)_{air}] \times [^{20}Ne_{sample}]/(^{20}Ne/^{22}Ne)_{sample}$, where $(^{21}Ne/^{22}Ne)_{air} = 0.0290$. ^{4}He is assumed to be totally radiogenic. The $^{4}He\text{-rad}/^{21}Ne\text{-excess}$ ratios for the analysed gases are much lower than the range for the production ratio in crustal rocks $(1–3) \times 10^7$ (Ballentine and Burnard 2002). Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

than those in the Carpathian region. This suggests that the Pomeranian gas reservoirs are older than Carpathian ones, or concentrations of parent nuclides producing ^{4}He and ^{40}Ar are higher in the Pomeranian than in the Carpathian regions, because abundances of radiogenic and nucleogenic noble gas isotopes in the reservoir depend on accumulation time and abundances of parent nuclides such as K, U and Th. Radiogenic $^{4}He/^{40}Ar$ ratios are in a narrower range of 7–22 and higher than those in the Carpathian region as shown in Fig. 9a. The ratios are higher than the average production rate ratio of about 5 for radiogenic $^{4}He/^{40}Ar$ in crustal materials (e.g. Ballentine and Burnard 2002). The high ratios might have been caused by selective supply of lighter isotope ^{4}He than ^{40}Ar from crustal rocks, or (U + Th)/K ratio might be higher than the average in crustal block.

Excess ^{21}Ne is also enriched in the gases (Fig. 9b) compared with those from the Carpathian gases (Kotarba and Nagao 2008). Most data points show $^{4}He_{rad}/^{21}Ne_{excess}$ ratios in a narrow range of $\sim 3 \times 10^7$, with two exceptions Gw-15 (1.7×10^7) and Se-1 (1.3×10^7) (see Table 6). The ratios are in the range of $(1–3) \times 10^7$ observed for gases with abundant radiogenic noble gases (e.g. Ballentine and Burnard 2002). Both radiogenic ^{4}He and nucleogenic ^{21}Ne are probably produced by a common source, where both the nuclear reactions of α-decay and (α, n) are occurring simultaneously. On the other hand, radiogenic ^{40}Ar is produced from ^{40}K-decay independently from the α-decay of U and Th. Consequently, the correlation between the radiogenic ^{4}He and ^{40}Ar productions would become obscure as compared to that of ^{4}He and ^{21}Ne. Another reason is a different diffusion rate between He and Ar in crustal rocks, resulting in decoupling between them. Concentrations of the

Table 6 $^{4}He/N_2$ and $^{20}Ne/N_2$ ratios, and radiogenic and nucleogenic isotopes

Sample code	N_2 (vol%)[a]	$^{4}He/N_2$	$(^{20}Ne/N_2)\ 10^{-8}$	$^{4}He_{rad}$ (ppm)	$^{21}Ne_{nucl}\ 10^{-5}$ (ppm)	$^{40}Ar_{rad}$ (ppm)	$(^{4}He/^{40}Ar)_{rad}$	$(^{4}He/^{21}Ne)_{rad}\ 10^{7}$
Eastern Pomerania								
Di-4	1.75	0.0690	46.6	1,210	4.0	102	11.8	3.02
Zc-8k	2.50	0.0452	26.1	1,130	3.4	58	19.4	3.31
Zc-IG4	0.76	0.1500	86.8	1,140	3.3	51	22.4	3.50
Western Pomerania								
Wo-11	43.1	0.00314	9.3	1,350	4.9	70	19.4	2.73
Gw-15	56.6	0.00389	5.7	2,200	12.9	205	10.7	1.70
Gw-31	52.7	0.00380	6.6	2,010	7.0	140	14.4	2.87
Do-21k	33.7	0.00283	5.3	952	2.5	63	15.1	3.76
Bd-10	50.3	0.00299	5.8	1,510	5.2	113	13.3	2.91
Co-2	48.5	0.00317	4.2	1,540	5.0	118	13.1	3.09
Se-1	46.1	0.00283	5.1	1,310	10.1	176	7.4	1.29

Rad radiogenic, *nucl* nucleogenic

[a] From Table 2

radiogenic and nucleogenic noble gases seem to be higher in Western Pomerania than in Eastern Pomerania, which may suggest an older formation age for the Western Pomeranian gas reservoirs.

Isotope ratios of Kr and Xe measured for three samples (Zc-8k, Gw-15 and Se-1) are summarized in Table 7. Isotope ratios are almost atmospheric within experimental error limits. A small excess in ^{136}Xe would be a product of spontaneous fission of ^{238}U. The fissiogenic ^{136}Xe concentrations plotted against radiogenic ^{4}He do not show clear positive correlation, which is expected if the progenitor for the fissiogenic ^{136}Xe and radiogenic ^{4}He is ^{238}U. The production rate ratio of $^{136}Xe_{fiss}/^{4}H_{rad} = 4.3 \times 10^{-9}$ calculated for ^{238}U is shown in Fig. 10, where 5.45×10^{-7} and 0.063 for branching ratio of spontaneous fission and yield of ^{136}Xe, respectively, were used (Ozima and Podosek 2002). The value is an upper limit for the observed $^{136}Xe_{fiss}/^{4}He_{rad}$ ratio because ^{4}He can also be produced from ^{235}U and ^{232}Th.

Carbon dioxide

Carbon dioxide concentrations in the analysed natural gases of Eastern and Western Pomerania vary from 0.83 to 0.93 vol% and from 0.02 to 0.17 vol% (Table 2), and $\delta^{13}C$ values of the carbon dioxide from −2.2 to −0.5 ‰ and from −16.4 to −6.7 ‰ (Table 3), respectively.

Natural carbon dioxide is generated in the course of various biogenic and abiogenic processes: oxidation of sedimentary organic matter, decarboxylation of lipids, microbial activity, thermogenic alteration of organic matter, chemical equilibrium among feldspar, clay and carbonate minerals in siliciclastic and carbonate reservoirs, hydrocarbon oxidation by mineralized waters, thermic (metamorphic) decarbonization of carbonates, carbonate hydrolysis and endogenic (mantle or volcanic) activities (Barry et al. 2013; Cooles et al. 1987; Farmer 1964; Gutsalo and Plotnikov 1981; Hutcheon and Abercrombie 1990; Imbus et al. 1998; Jenden et al. 1993; Kotarba 1988, 2001, 2012; Kotarba and Rice 2001; Pankina et al. 1978; Seewald 2003; Smith and Ehrenberg 1989, and references therein). Moreover, secondary processes during migration as water solution also cause isotope fractionation (e.g. Hałas et al. 1997; Leśniak and Zawidzki 2006). Lewan (1997) attributes the high CO_2 generation in hydrous pyrolysis to the interaction of water with oxygen-bearing functional groups in the bitumen and with dissolved water in the bitumen.

The plot of $\delta^{13}C(CO_2)$ versus $\delta^{13}C(CH_4)$ (Fig. 11a) suggests that carbon dioxide in the Middle Cambrian reservoir of Eastern Pomerania was mainly generated during thermal transformation of organic matter and that apart from the thermogenic component, gases from Mississippian (Wo-11), Pennsylvanian and Rotliegend (Bd-10), and Rotliegend (Se-1) reservoirs of Western Pomerania can also contain an endogenic component.

$C(CO_2)/^{3}He$ ratios are plotted against the $\delta^{13}C(CO_2)$ in Fig. 11b, where typical values for MORB source, marine carbonate and organic sediments are shown for comparison (Sano and Marty 1995). The data obtained for the Carpathian gases (Kotarba and Nagao 2008) also plotted here have $C(CO_2)/^{3}He$ ratios of the order of 10^{8}, which is lower than the MORB value, $C(CO_2)/^{3}He = 1.5 \times 10^{9}$, although their $\delta^{13}C(CO_2)$ values scatter between those for biogenic and mantle sources. By comparison, those for Western Pomerania show clearly lower $C(CO_2)/^{3}He$ ratios in the range from 10^{6} to 10^{7} and $\delta^{13}C(CO_2)$ similar to MORB value. Data points for Eastern Pomerania are except the Western Pomerania area, i.e. both $C(CO_2)/^{3}He$

Table 7 Kr and Xe isotopic ratios

Sample code	Isotopes															
	^{78}Kr	^{80}Kr	^{82}Kr	^{83}Kr	^{84}Kr	^{86}Kr	^{124}Xe	^{126}Xe	^{128}Xe	^{129}Xe	^{130}Xe	^{131}Xe	^{132}Xe	^{134}Xe	^{136}Xe
Eastern Pomerania															
Zc-8k	0.00601 ± 0.00021	0.04041 ± 0.00055	0.2023 ± 0.0021	0.2003 ± 0.0015	=1	0.3029 ± 0.0017	0.00403 ± 0.00045	0.00344 ± 0.00039	0.0718 ± 0.0041	0.9885 ± 0.0097	0.1527 ± 0.0044	0.7909 ± 0.0130	=1	0.3903 ± 0.0061	0.3368 ± 0.0059
Western Pomerania															
Gw-15	0.00604 ± 0.00011	0.04014 ± 0.00046	0.2042 ± 0.0015	0.2015 ± 0.0018	=1	0.3030 ± 0.0015	0.00376 ± 0.00039	0.00341 ± 0.00035	0.0716 ± 0.0018	0.9953 ± 0.0090	0.1539 ± 0.0028	0.7850 ± 0.0091	=1	0.3898 ± 0.0061	0.3358 ± 0.0044
Se-1	0.00646 ± 0.00034	0.04014 ± 0.00092	0.2026 ± 0.0033	0.2018 ± 0.0024	=1	0.3029 ± 0.0028	0.00355 ± 0.00023	0.00342 ± 0.00064	0.0733 ± 0.0022	0.9899 ± 0.0183	0.1513 ± 0.0050	0.7918 ± 0.0143	=1	0.3982 ± 0.0090	0.3423 ± 0.0080
Air[a]	0.006087 ± 0.000020	0.03960 ± 0.00002	0.20217 ± 0.00004	0.20136 ± 0.00021	=1	0.30524 ± 0.00025	0.003537 ± 0.000011	0.003300 ± 0.000017	0.07136 ± 0.00009	0.9832 ± 0.0012	0.15136 ± 0.00012	0.78900 ± 0.00110	=1	0.38790 ± 0.00060	0.32940 ± 0.00040

[a] After Ozima and Podosek (2002)

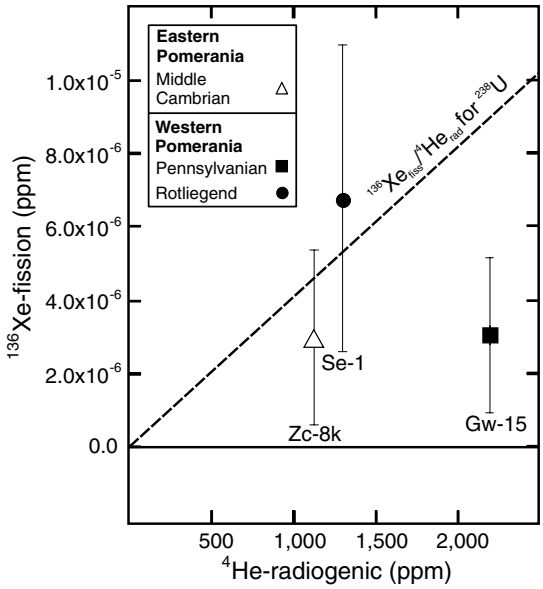

Fig. 10 ^{136}Xe-fission versus radiogenic ^{4}He for three selected samples of natural gases accumulated in Middle Cambrian, Pennsylvanian and Rotliegend reservoirs. Concentration of fissiogenic ^{136}Xe was calculated by $[^{136}Xe_{fiss}] = [(^{136}Xe/^{130}Xe)_{sample} - (^{136}Xe/^{130}Xe)_{air}] \times [^{130}Xe]$, where $(^{136}Xe/^{130}Xe)_{air} = 2.176$. Broken line represents production rate ratio of $^{136}Xe_{fiss}/^{4}He_{rad} = 4.3 \times 10^{-9}$ calculated for ^{238}U. The slope shows an upper limit because ^{4}He can also be produced from ^{235}U and ^{232}Th. For key for samples, see Table 1

(in order of 10^8) and $\delta^{13}C(CO_2)$ (~0 ‰) values are higher in the latter area than the former one. The low and scattered ratios for gases from both the Pomeranian and Carpathian regions may be explained by the thermogenic origin of carbon dioxide mentioned above, and the origins of ^{3}He and CO_2 in the source regions are decoupled. Carbonates do not occur in the Palaeozoic strata of Eastern and Western Pomerania. However, it cannot be excluded that carbon dioxide was also at least partly originated during thermal decomposition of carbonates because they probably occur in Precambrian profile. Carbon dioxide from the Carpathian region contains thermogenic and also microbial components (Kotarba and Nagao 2008).

Nitrogen

Nitrogen concentration in analysed natural gases in the Middle Cambrian (Eastern Pomerania) and Carboniferous-Lower Permian (Western Pomerania) reservoirs varies from 0.76 to 2.50 vol% and from 33.7 to 56.6 vol% (Table 2), respectively. δ^{15}N values of the molecular nitrogen vary from −12.9 to −12.4 ‰ and from 5.2 to 11.2 ‰ (Table 3), respectively.

Nitrogen is produced in great quantities during the thermogenic transformation of organic matter both from humic and sapropelic organic matter (Kotarba 1988; Krooss et al.

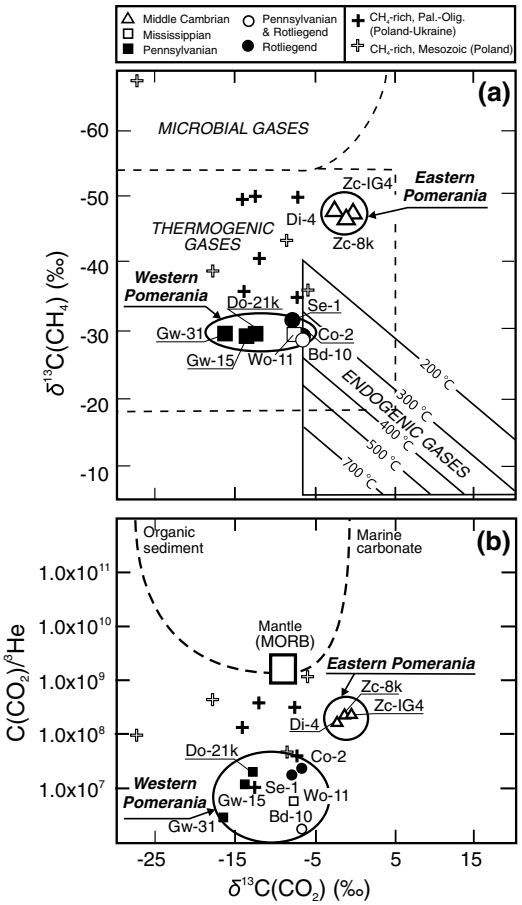

Fig. 11 **a** $\delta^{13}C(CH_4)$ and **b** $C(CO_2)/^3He$ versus $\delta^{13}C(CO_2)$ for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. Compositional fields **a** modified from Gutsalo and Plotnikov (1981) and Kotarba (1988) and **b** after Sano and Marty (1995). Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

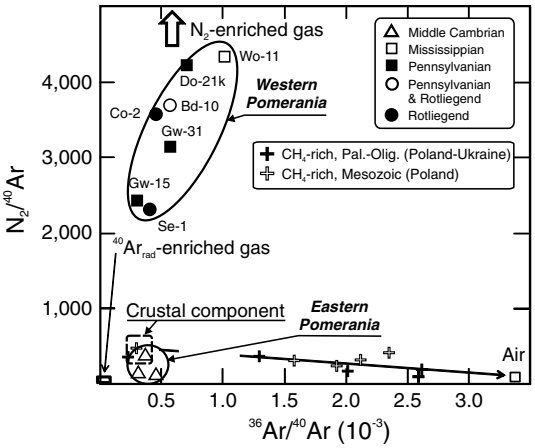

Fig. 12 $N_2/^{40}Ar$ versus $^{36}Ar/^{40}Ar$ for natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. The *square* labelled "Crustal component" in the figure shows the area encompassing data points for gas fields in USA and the *rectangle* at the lower right corner indicates N_2/Ar ratio for air (84) and for fractionated air dissolved in water (~40) (Ballentine and Sherwood Lollar 2002). Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

1995; Littke et al. 1995; Maksimov et al. 1982) and/or from NH_4-rich illites that had undergone intensive fluid/rock interaction (Mingram et al. 2005; Lüders et al. 2005). The process of molecular nitrogen production from organic matter was also documented by pyrolysis experiments (Gerling et al. 1997; Kotarba and Lewan 2013). $\delta^{15}N$-values of nitrogen of natural gases range from −15 to 18 ‰ (Gerling et al. 1997). This isotopic fractionation results from primary genetic factors and secondary processes taking place during migration at the gas–rock and gas-reservoir fluids interface (Stahl 1977; Gerling et al. 1997; Krooss et al. 2005; Littke et al. 1995; Mingram et al. 2005; Lüders et al. 2005; Zhu et al. 2000).

$N_2/^{40}Ar$ is plotted against $^{36}Ar/^{40}Ar$ in Fig. 12, according to Ballentine and Sherwood Lollar (2002). Ballentine and Sherwood Lollar (2002) describe that N_2 might have been produced in crust through devolatilization of low-grade metamorphic rocks or denitrification of a relatively mature marine source rock. The low $^{36}Ar/^{40}Ar$ ratio for the samples also could have resulted from the accumulation of ^{40}Ar produced from ^{40}K. The rectangle at the lower right corner in Fig. 12 indicates the N_2/Ar ratio for air (84) and for air dissolved in water (~40). The samples from Eastern Pomerania plot close to but slightly lower than those for gases from the USA fields, suggesting a similar origin. Although most samples in Kotarba and Nagao (2008) were plotted between the crustal production and atmospheric components, which can be explained as dilution of original gases with atmospheric Ar and N_2, no other data indicate such an addition of atmospheric gases. The low molecular nitrogen concentrations and their strong negative $\delta^{15}N$-values (Fig. 13a) in gases from the Cambrian reservoir of Eastern Pomerania may suggest that it was partly derived from NH_3 and NH_4 of crustal fluid. The stable nitrogen isotope fractionation between NH_3 and NH_4 was described by Urey (1947) and Hermes et al. (1985). In lower scale, this mode of N_2 generation is also possible for gases of Western Pomerania. The mobilized nitrogen mainly migrated as NH_3/NH_4 within the Carboniferous strata and was oxidized to N_2 and Fe^{3+} during upward migration through the red beds of Rotliegend profile (Hoth et al. 2002). In contrast to the gases from Eastern Pomerania, the samples from Western Pomerania are greatly enriched in N_2 compared with the crustal component. This may be caused by inflow of thermogenic nitrogen.

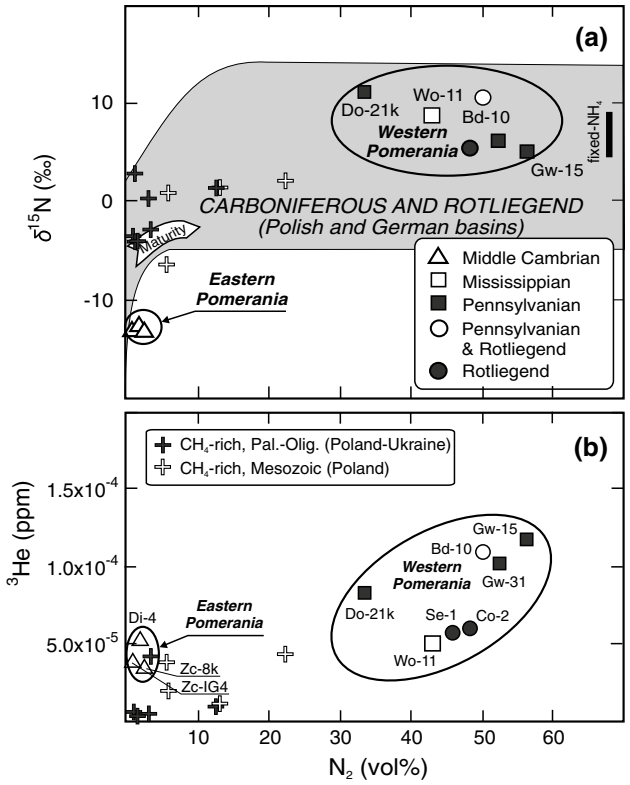

Fig. 13 **a** $\delta^{15}N$ of molecular nitrogen and **b** ^{3}He concentration versus N_2 concentration of natural gases accumulated in Middle Cambrian, Mississippian, Pennsylvanian and Rotliegend reservoirs. **a** Direction of maturity of source rock and data for Pennsylvanian and Rotliegend gases of Polish and German basins after Gerling et al. (1997) and $\delta^{15}N$ range of fixed-NH_4 in rich illites after Mingram et al. (2005) and **a**, **b** Mesozoic and Palaeocene–Oligocene gases from the Polish and Ukrainian Carpathian region after Kotarba and Nagao (2008). For key for samples, see Table 1. *Pal.* Palaeocene, *Olig.* Oligocene

Concentrations of ^{3}He versus N_2 are presented in Fig. 13b, where the areas for Eastern and Western Pomerania are distinctly separated from each other. Concentrations of both ^{3}He and N_2 in Eastern Pomerania as well as those for the Carpathian region (Kotarba and Nagao 2008) are low compared to the samples from Western Pomerania. The weak positive correlation between ^{3}He and N_2 concentrations can be probably attributed to the volcanic activity that occurred in the Western Pomerania region during late Stephanian–early Rotliegend (Autunian) ages. The volcanic activity supplied ^{3}He and heat from the mantle, resulting in the accumulation of mantle-derived ^{3}He and thermogenic N_2 in the source region of the gases. The low ^{3}He and N_2 concentrations in gases from Eastern Pomerania and from the Carpathian region (Kotarba and Nagao 2008) reflect a weak effect of volcanic activity on these areas.

The general increasing trend of $\delta^{15}N(N_2)$ values with N_2 concentration (Fig. 13a) suggests that molecular nitrogen from Eastern Pomeranian natural gases was mainly generated during low-temperature thermal transformation of organic matter and has crustal component (Fig. 12), whereas molecular nitrogen from Western Pomeranian natural gases containing significant component from decomposition of organic matter at higher maturity level may have been caused by high heat flux from the volcanic activity during late Stephanian–early Rotliegend (Autunian) ages. Moreover, molecular nitrogen of gases from Western Pomerania has a bigger component release from NH_4-rich illites of the clayey facies than gases from Eastern Pomerania (Fig. 13a).

Conclusions

Analyses of molecular and stable isotope compositions of carbon in methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane and carbon dioxide, of hydrogen in methane, of nitrogen isotope in molecular nitrogen, and stable isotope composition of noble gases (helium, neon, argon, krypton and xenon) of natural gases associated with oil from Middle Cambrian reservoir in Eastern Pomerania and non-associated gases from Mississippian, Pennsylvanian and Rotliegend (Lower Permian) strata in Western Pomerania of the Polish Baltic region reveal the following:

1. Molecular and isotopic compositions in gases from Eastern Pomerania and Western Pomerania are clearly different, which likely reflects their different tectonic setting and genetic type of source organic matter.
2. Hydrocarbon gases, associated with oil accumulated in the Middle Cambrian reservoir of Eastern Pomerania, are genetically related to thermogenic processes and were generated during low-temperature thermogenic processes ("oil window") from only one source rock containing Type-II kerogen at maturity corresponding to 0.5–0.7 % vitrinite reflectance scale.
3. Non-associated hydrocarbon gases accumulated in the Mississippian, Pennsylvanian and Rotliegend reservoirs of Western Pomerania are genetically related with thermogenic processes of mainly Type-III kerogen and small components of mixed Type-III/II kerogen. At least two phases of gas generation took place: the first one at the stage corresponding to 0.7–0.9 % and the second one corresponding to 1.5–2.0 % vitrinite reflectance scale.
4. Noble gases are, in general, heavily enriched in radiogenic and nucleogenic isotopes such as ^{4}He, ^{40}Ar and ^{21}Ne accumulated in the reservoirs. Weak contributions of mantle-derived He and Ne are observed.
5. Radiogenic $^{4}He/^{40}Ar$ ratios are higher than the average production rate ratio of about 5 for radiogenic $^{4}He/^{40}Ar$ in crustal materials, which may have been caused by

selective supply of lighter isotope ^{4}He than ^{40}Ar from crustal rocks, or a (U + Th)/K ratio or (U + Th)/K ratio might be higher than the average in crustal block.

6. Carbon dioxide from gases of both Western and Eastern Pomerania was mainly generated during thermogenic processes of transformation of organic matter, although gases from Mississippian (Wo-11), Pennsylvanian and Rotliegend (Bd-10), and Rotliegend (Se-1) reservoirs of Western Pomerania can contain endogenic component.
7. Molecular nitrogen from Eastern Pomeranian natural gases was mainly generated during low-temperature thermal transformation of organic matter and derived from NH_3 and NH_4 of crustal fluid.
8. The molecular nitrogen encountered in Western Pomeranian reservoirs was generated from decomposition of organic matter of higher maturity level. Accelerated thermogenic production of N_2 may have been caused by high heat flux from volcanic activity during late Stephanian–early Rotliegend (Autunian) ages. Moreover, this nitrogen can have a higher proportion originating from NH_4-rich illites than in Eastern Pomerania natural gases.

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